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14. ABSTRACT

A state-of-the-art, metal-organic chemical vapor deposition (MOCVD) system was acquired and successfully installed. The instrumentation is capable of growth of group-III nitride alloys with control down to the atomic level. The new system has been used to grow novel gallium nitride nanowires, including gallium nitride/indium-gallium nitride/p-type gallium nitride core/shell/shell heterostructures. Structural measurements demonstrate the successful growth of these new nanomaterials, and moreover, physical measurements demonstrate that these new nanowire heterostructures enable high-efficiency blue nanoscale light-emitting diodes.

15. SUBJECT TERMS

Metal-Organic Chemical Vapor Deposition; MOCVD; Nanowires; Gallium Nitride; Photonics

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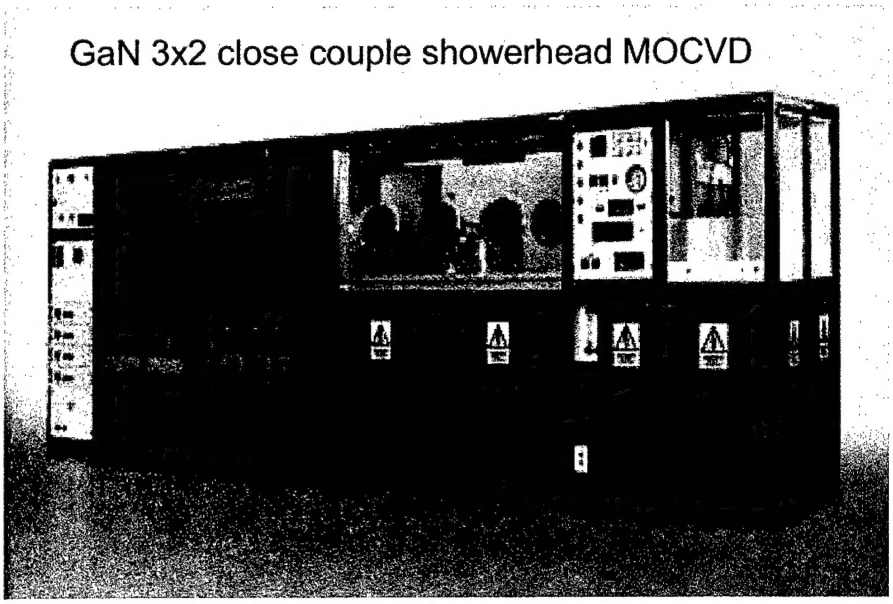
I. Summary of Equipment Acquired.

Equipment	Manufacturers	Cost ($)
3x2 CCS MOCVD system	Thomas Swan Scientific Equipment, MOCVD	$68,900
Gas Cabinets for MOCVD	Stainless Design Concepts	$ 65,700
Gas Detectors for MOCVD	Zellweger Analytics, Inc.	$ 5,400
MS/Mass Spec System	Thermo Finnigan LLC	$ 80,000
Institutional Cost Sharing (for MS/Mass Spec System)	Thermo Finnigan LLC	$ 150,000
Total Cost of Instrumentation		**$ 370,000**

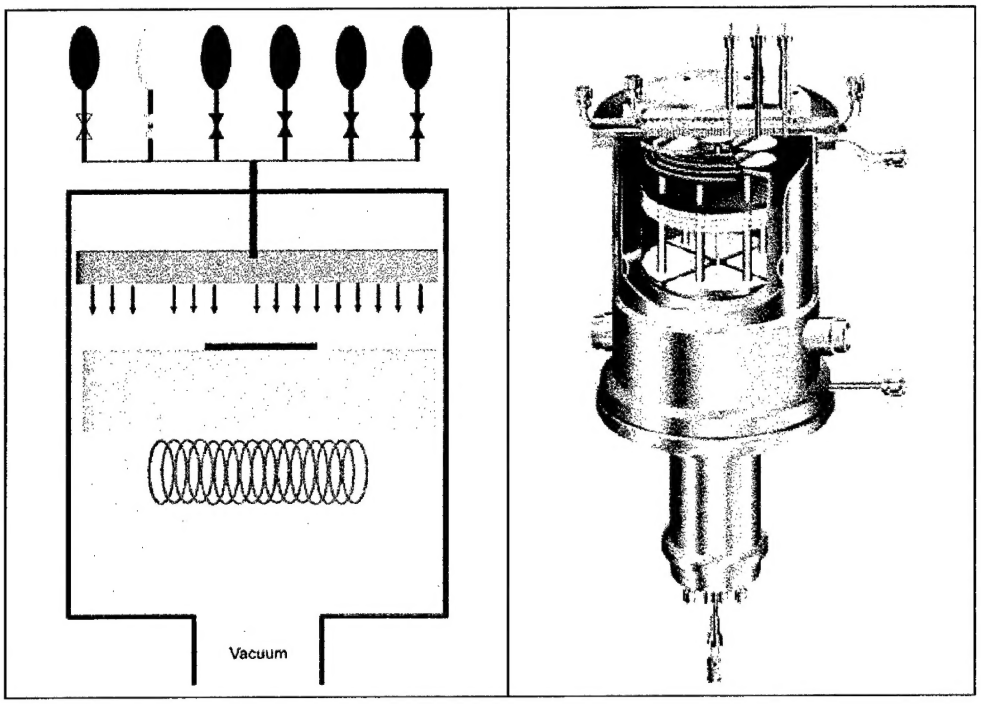
II. Summary of Research and Education Utilizing DURIP Equipment.

The intial phase of the DURIP grant was focused on the installation and testing of the metal-organic chemical vapor deposition (MOCVD) instrument and supporting equipment. The equipment is now located in a laboratory that was renovated by the University to support this new instrumentation. The main instrument shown below



includes an integrated gas delivery system (left portion of system), which enables precise control of metal-organics and other gases without mixing prior to delivery to the growth substrate, and a reactor that is contained within a high-purity glove-box with sample substrate loadlock (center/right portion of system). The entire system is operated under computer control, which enables precise and repeatable variation in all of the key reaction variables including partial pressure of reactants, temperature and pressure. The reactor

itself was chosen to meet the unique requirements of the proposed AFOSR nanomaterials research. The reactor design is shown schematically (left) and as cut-away view (right) below.

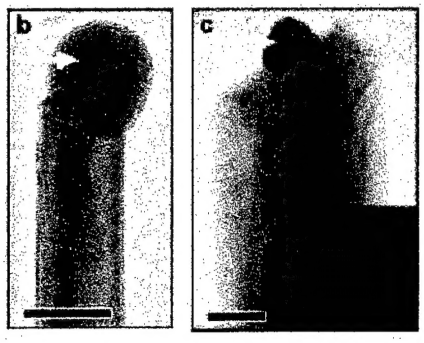


A key feature of the chosen reactor, which is water cooled and close-coupled to the growth substrate, is that it enables delivery of complex mixtures of metal-organic compounds to the heated growth substrate with little or no pre-reaction. Overall, this capability is central to our focus on the designed and rational synthesis of complex and functional nanomaterials.

Significantly, this instrumentation has made very significant impact on the P.I.'s AFOSR-funded research program by enabling the growth of novel gallium nitride based nanowires for the first time. We have focused on GaN-based materials since alloys of (Al-Ga-In)N are direct band gap semiconductors with potential for light emission from the ultraviolet through visible regions of the electromagnetic spectrum. Previous studies of planar LEDs have shown that n-GaN/InGaN/p-GaN and related double heterostructures exhibit enhanced light emission efficiency compared to simple n-GaN/p-GaN diode structures, and thus suggest that CSS versus core/shell (CS) structures would be ideal candidates for GaN-based active nanowire devices. The nanowire CSS structures also have potentially significant differences compared to planar heterostructures beyond that of dimensionality. In particular, because nanowire synthesis is essentially substrate-free it should prevent formation of dislocations originating from lattice mismatch between GaN and growth substrates, and thereby reduce nonradiative recombination (at these defects) relative to planar structures.

Our approach for preparing the GaN-based CSS structures involves initial metal nanocluster mediated vapor-liquid-solid (VLS) growth of an n-type GaN core followed by sequential radial growth of intrinsic InGaN and p-type GaN shells. Scanning electron

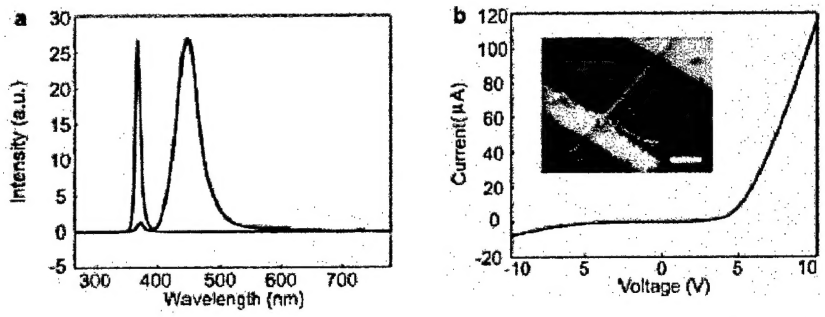
microscopy (SEM) images of Si-doped GaN nanowires obtained following axial elongation reveal a high yield of uniform nanowire cores. A bright field transmission electron microscopy (TEM) image of a representative n-GaN core (Fig. b) shows that the nanowire diameter is essentially the same as the nickel nanocluster diameter as expected for the VLS process. Corresponding TEM images of n-GaN/InGaN CS nanowires demonstrate that the overall diameters increase following InGaN shell growth. Examination of a representative CS nanowire end (Fig. c) shows that the overall diameter is substantially larger than that of the nanocluster, in contrast to the core nanowires (Figure 2b), and that the nanowire has a triangular cross-section. Energy dispersive X-ray spectroscopy (EDX) mapping (inset, Figure c) demonstrates that nanoclusters at the CS nanowire ends are nickel while the larger core-shell nanowire structure contains Ga, In and N. Taken together, these results strongly suggest that shell growth is epitaxial as required for efficient devices.



High-resolution TEM and EDX were used to characterize in greater detail the CS and CSS nanowires. Lattice-resolved images obtained from n-GaN/InGaN/p-GaN CSS nanowires containing a nominal 20% In in the InGaN shell demonstrate that the CSS nanowires have a single crystalline structure, while lower resolution bright-field images show no evidence of either dislocations or other defects following growth of the inner InGaN and outer p-GaN shells; these results imply that strain at the GaN/InGaN interface is not relaxed. To characterize the CS and CSS nanowires further we recorded and analyzed EDX compositional line profiles. Overall, the EDX data shows clearly distinct differences in the spatial profiles of In and Ga that are qualitatively consistent with well-defined InGaN shells in the CS and CSS structures. Taken together these TEM and EDX studies provide strong evidence for the growth of single crystal GaN/InGaN CS and GaN/InGaN/GaN CSS nanowire structures with well-defined and controllable shell thicknesses and composition.

We have recently characterized the GaN-based CSS nanowires further by optical, electrical and optoelectronic measurements. Photoluminescence (PL) spectra recorded on n-GaN and n-GaN/InGaN/p-GaN CSS nanowire structures (Fig. a) demonstrate the excellent crystalline quality of the n-GaN core. Significantly, the PL spectra obtained from n-GaN/InGaN/p-GaN CSS structures show a dominant emission peak at 448 nm. This wavelength is consistent with band-edge emission from an InGaN structure of composition $In_{0.18}Ga_{0.82}N$. The InGaN emission is ca. 20 times stronger than the small GaN band-edge emission peak also present in the PL spectrum, which shows that the much smaller volume InGaN shell in our CSS structures provides an efficient region for radiative recombination. These PL data show that impurity or defect-related emission at wavelengths longer than the InGaN band-edge peak are not significant, and thus demonstrate that the CSS nanowires have very good optical quality. In addition, the n-GaN/InGaN/p-GaN CSS nanowire heterostructures have been used to prepare functional nanoscale LEDs. Electrical transport measurements made in a field-effect transistor configuration demonstrate that the Si-doped GaN nanowires and the Mg-doped GaN

outer shells of the CSS nanowires are n-type and p-type, respectively. These results are consistent with our previous studies of homogeneous n-



and p-type nanowires, and planar materials. Simultaneous electrical contacts to both the n-type core and p-type outer shell of individual CSS nanowires, which are required to inject electrons and holes into the InGaN quantum well, were achieved using a focused ion beam microscope to etch and expose selectively the core at one end of the CSS nanowires (inset, Fig. b). Significantly, current versus voltage data recorded between contacts to the n-type core and p-type shell (Fig. 4b) show current rectification with a sharp onset at ca. 4 V in forward bias that is characteristic of a p-n diode. Notably, the electroluminescence (EL) spectrum collected from forward biased n-GaN/InGaN/p-GaN CSS nanowire devices exhibit an intense peak in the 440-460 nm range that is in good agreement with the PL spectra recorded from similar CSS nanowires. These results show that injected electrons and holes recombine in an InGaN active shell in these new nanowire heterostructures.

Lastly, this new instrumentation has provided substantial new educational opportunities for graduate students working on the AFOSR funded project. The state-of-the-art growth system provides unique introduction to an essential system for nanomaterials growth that will be critical to developing human infrastructure for leading DoD research in nanoscience and nanotechnology in the future.

Reference

F. Qian, Y. Li, S. Gradecak, D. Wang, C. J. Barrelet & C. M. Lieber, Gallium Nitride-Based Nanowire Radial Heterostructures for Nanophotonics. *Nano Lett.*, submitted for publication.